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Organic ultraviolet photovoltaic diodes based on copper phthalocyanine as an electron acceptor

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Abstract

Organic ultraviolet (UV) light-sensitive photovoltaic (PV) diodes, based on 4, 4′, 4″-tris-(2-methylphenyl phenylamino) triphenylamine (m-MTDATA) as an electron donor and copper phthalocyanine (CuPc) as acceptor, have been fabricated. The PV diode exhibits high open-circuit voltage (V_{OC}) of 1.05 V under illumination of 365 nm UV light with 1.7 mW/cm^2, although the CuPc was generally used as electron donor in other PV diodes. And the short-circuit current (I_{SC}) of 54.6 μA/cm^2, fill factor (FF) of 0.304 and power conversion efficiency (η_e) of 1.03% are respectively achieved. This diode can accurately detect the UV radiation according to photo-generated voltage signal.
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Keywords: Organic; Ultraviolet; Photovoltaic diodes; Copper phthalocyanine

1. Introduction

As small molecule organic semiconductors, phthalocyanines (Pcs) are currently under intensive investigation due to their potential use in a variety of organic electronic and optoelectronic devices, such as field effect transistors [1], organic light-emitting diodes (OLEDs) [2], photovoltaic (PV) cells [3–5] and photo-detectors [6]. Their thermally stable

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nature makes them suitable for thin film deposition processes by thermal evaporating. Copper phthalocyanine (CuPc) has been widely used both as hole-injection material in OLEDs and as electron donor in PV cells due to its better hole-transporting ability. However, low open-circuit voltage (V_{OC}), such as V_{OC} of 450 mV [3] under "one-sun" illumination and V_{oc} of 480 mV [5], has been reported, respectively, although the PV diodes have higher short-circuit current (I_{SC}).

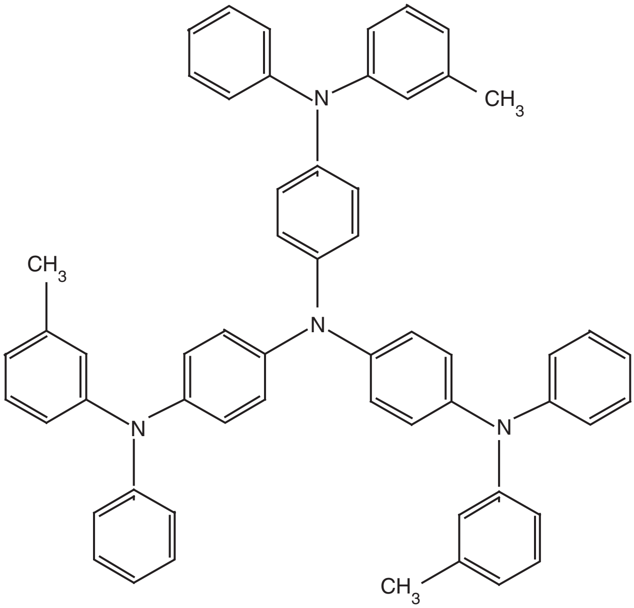
Because electron mobility in CuPc at an electric field of 4×10^5 V/cm is 9.04×10^{-4} cm^2/V s which is about two orders of magnitude larger than that of the typically electron transport (ET) material tris-(8-hydroxyquinoline) aluminum (Alq_3) at the same electric field (1.4×10^{-6} cm^2/V s) [7,8], the ET character of CuPc was considerably paid attention [9]. Hung et al. achieved voltage reduction in OLED using CuPc as ET layer to enhance electron injection. But electroluminescence (EL) efficiency was reduced because of higher-energy barrier (0.5 eV) between CuPc and emissive layer, Alq_3 [8]. Another application of ET characteristics of CuPc in OLED was reported by Lee [9], in which CuPc was used to increase the contrast ratio of EL emission display of OLEDs, but the UV-sensitized diode based on CuPc as ET layer is few reported. Although several types of UV-diodes have been developed using pn- or Schottky-junction diodes of inorganic semiconductors, such as GaN, ZnS and diamond and so on, UV-sensors based on organic materials are preferable due to their advantages with simpler fabrication processes and lower cost than those of inorganic devices.

In this context, PV performances of the organic devices based on 4, 4′, 4″-tris-(2-methylphenyl phenylamino) triphenylamine (m-MTDATA) as an electron donor and CuPc as electron acceptor were studied. The *I–V* characteristics under UV illumination and in the dark, the dependence of the PV performance on the film thickness of the materials, electron donor, incident UV-light density and the temperature were discussed.

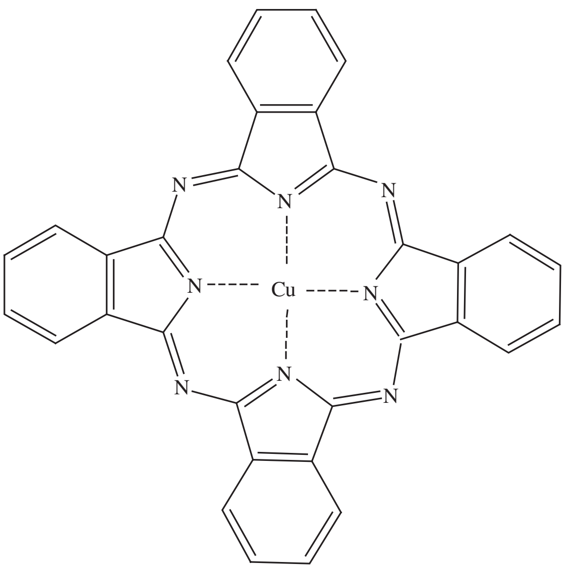
CuPc and m-MTDATA are respectively used as the electron acceptor and donor materials to construct organic PV diode for using UV-detector because CuPc has higher electron mobility and m-MTDATA has lower solid ionization potential (IP) (1.9 eV) [10] and higher hole transporting (HT) property [11]. The PV diodes based on m-MTDATA as electron donor have been studied in our group [12]. Because LUMO and HOMO of m-MTDATA are all considerably larger than that of CuPc [13,14], so the diode made up of m-MTDATA and CuPc should exhibit good PV effect. Poly (3,4-ethylene dioxythiophene): poly (styrene sulfonate) (PEDOT: PSS) has been reported to facilitate hole injection and to increase the built-in potential [4]. LiF is used as an electron injector in combination with an aluminum cathode. Thus, diode based on CuPc as an electron acceptor was designed and its PV performances were studied in detail. The device is with structure of ITO/PEDOT: PSS (20 nm)/m-MTDATA (30 nm)/CuPc (60 nm)/LiF (1 nm)/Al (100 nm), although CuPc as organic material has been used as hole injection layer in OLED [2] and as electron-donor in organic PV devices [3–5], respectively. The molecular structures of the organic materials used in this study are shown in Fig. 1.

2. Experiment

All of the materials were commercially available and used without further purification. A pre-patterned indium tin oxide (ITO) coated glass substrate with a sheet resistance of $20\,\Omega/\square$ was cleaned by acetone, glass detergent sonication and deionized water rinse. After UV ozone treatment for 10 min [15], the ITO substrates were overlay with PEDOT: PSS by



m-MTDATA



CuPc

Fig. 1. Chemical structure of organic materials used in this study.

spin coating then drying in a vacuum oven at 120 °C for 1 h. ITO substrates were loaded into a vacuum chamber and all the organic layers, LiF and Al cathode were sequentially deposited onto the ITO substrates by thermal evaporation at a pressure of 2×10^{-4} Pa without breaking the vacuum. The thickness of depositing film of above materials was monitored by a quartz oscillators and controlled at a rate of 0.2–0.4 nm/s for the organic layers and LiF, and 1.0 nm/s for the Al layer, respectively. The active area of typical device was 10 mm^2. Absorption spectra of all organic films on ITO substrate were measured with a Shimadzu UV-3101PC spectrophotometer. Photocurrent response curves were recorded under a 40 $\mu W/cm^2$ Xe lamp. All measurements were carried out in ambient air at room temperature without being especially pointed out.

3. Results and discussion

3.1. Photocurrent response and absorption spectra

Fig. 2 indicates photocurrent response curve of the device with the structure ITO/PEDOT: PSS (20 nm)/m-MTDATA (30 nm)/CuPc (60 nm)/LiF (1 nm)/Al (100 nm), from which we noticed that the response wavelength is mainly located from 300 to 420 nm peaked at 360 nm, which is mostly corresponding to the UV light absorption of both m-MTDATA and CuPc films because the absorption of m-MTDATA/CuPc double layer films is added up by the two composed films (see the inset). The photocurrent response curve at longer wavelength should be resulted from contribution of the CuPc due to its absorption between 500 and 700 nm. This finding demonstrates that photo-generated excitons should be created in both the m-MTDATA and CuPc layers according to the photocurrent response curve.

3.2. The selecting of the film thickness of the organic materials

Dependence of V_{oc} on the film thickness of PEDOT: PSS, m-MTDATA and CuPc components of the PV device were studied, as depicted in Fig. 3, and it is seen that the

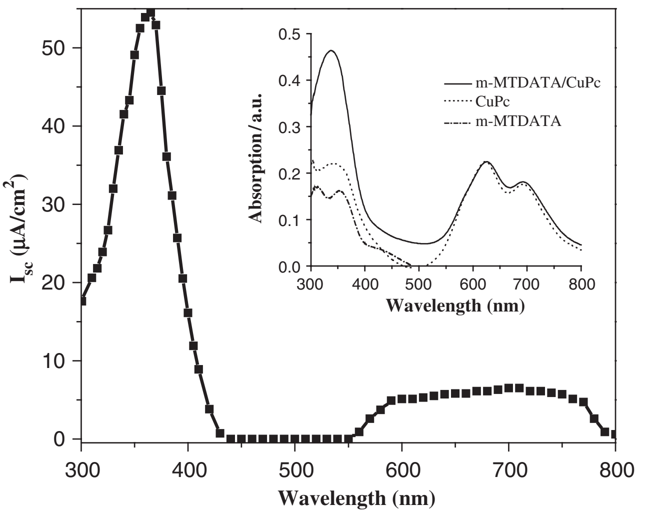


Fig. 2. Photocurrent response curve of the device ITO/PEDOT: PSS (20 nm)/m-MTDATA (30 nm)/CuPc (60 nm)/LiF (1 nm)/Al (100 nm). (Inset): Absorption spectra of the m-MTDATA film, CuPc film and m-MTDATA/CuPc film.

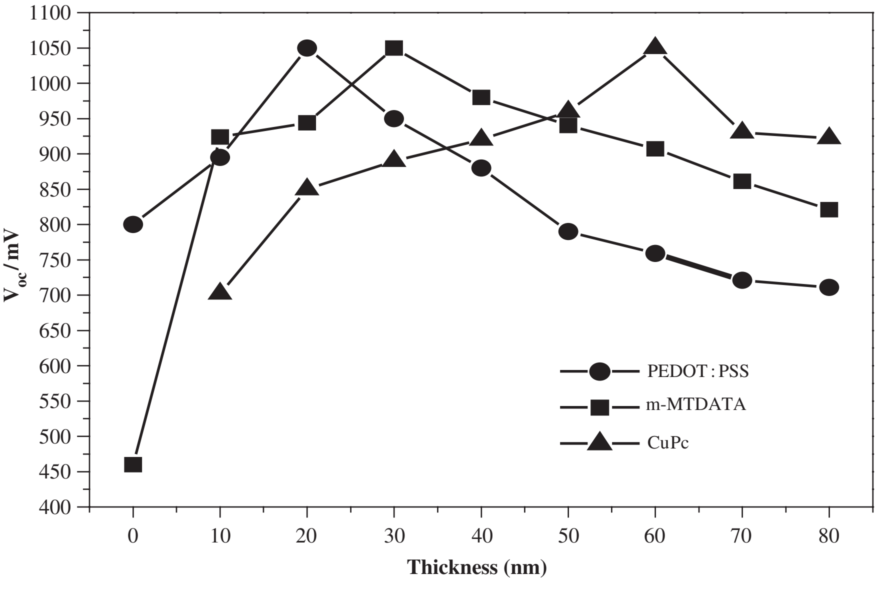


Fig. 3. Variation of V_{OC} with film thickness of respective layers of PEDOT: PSS, m-MTDATA and CuPc.

better performances of the device were achieved when the film thickness of PEDOT: PSS, m-MTDATA and CuPc were fixed at 20, 30, 60 nm, respectively.

3.3. The performance of the photovoltaic device

Fig. 4(a) shows the I–V characteristics of the diode under dark (UV-off) and under UV (365 nm) illumination with total power density of 1.7 mW/cm^2 (UV-on). It is found that the device ITO/PEDOT: PSS (20 nm)/m-MTDATA (30 nm)/CuPc (60 nm)/LiF (1 nm)/Al (100 nm) shows short-circuit current (I_{sc}) of 54.6 μA/cm^2, open-circuit voltage (V_{oc}) of 1.05 V, fill factor (FF) of 0.304, and power conversion efficiency η_e of 1.03%, respectively. Thus, it is concluded that the diode shows almost no signal under dark, but under illumination with the UV light it exhibits higher V_{oc} and larger I_{sc}, we can also say that the UV radiation can be easily detected by such a high V_{oc}, so it is demonstrated that the UV-diode can be applied as an UV-light sensitizing diode.

3.4. The effect of the electron donor on device performances

In order to account for excellent donating role of m-MTDATA in above PV device (a), other devices of ITO/PEDOT: PSS (20 nm)/TPD (x nm)/CuPc (60 nm)/LiF (1 nm)/Al (100 nm) was also constructed. When x is changed from 10, 20, 30 to 40, the I_{sc} is 9.7, 13.6, 20 and 10.7 μA/cm^2 respectively, so the device achieves better performance as the thickness of TPD is 30 nm (device b). Then effects of electron donor on the devices performances are listed in Table 1, and highest V_{oc}, I_{sc}, FF and η_e are determined also as shown in Fig. 4(b). The performance of device (a) is much better than that of device (b). It can be made clear from the energy bands [16,17] of the donor and acceptor as well as the PV processes

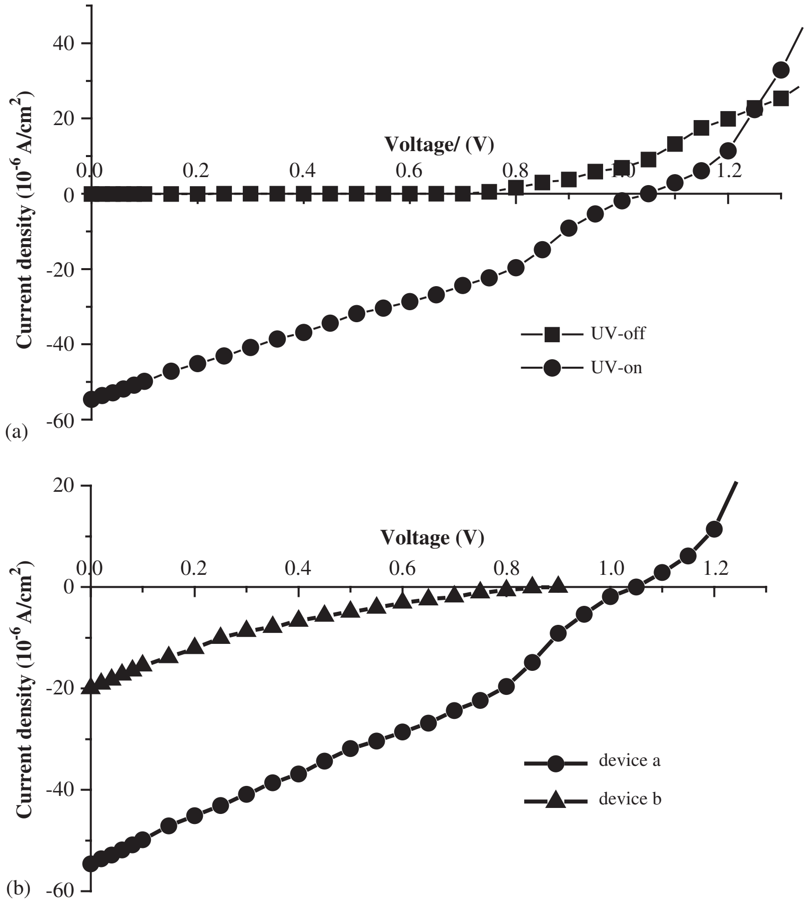


Fig. 4. (a) *I–V* characteristics of the device under dark (UV-off) and UV-illumination (UV-on), (b) *I–V* curves of two PV devices under UV light irradiance with 1.7 mW/cm^2.

Table 1
Effects of different electron donor on the device performances

Device	I_{sc} (10^{-6} A/cm^2)	V_{oc} (V)	FF	η_e (%)
(a)	54.6	1.05	0.304	1.03
(b)	20.0	0.88	0.260	0.27

indicated in Fig. 5, from which it is clear that after absorbing an incident photon, a hole in the HOMO and an electron in LUMO are respectively created in m-MTDATA donor and CuPc acceptor simultaneously, and then a bound electron–hole pair, i.e. exciton is formed (a). Subsequently, the photo-generated excitons diffuse to the D–A interface (b) to dissociate, through which a hole in the HOMO of the donor and an electron in the LUMO of the acceptor molecule are created (c). At last, driven by the built-in electric field, the photogenerated charge carriers transport to their respective electrodes and are collected by

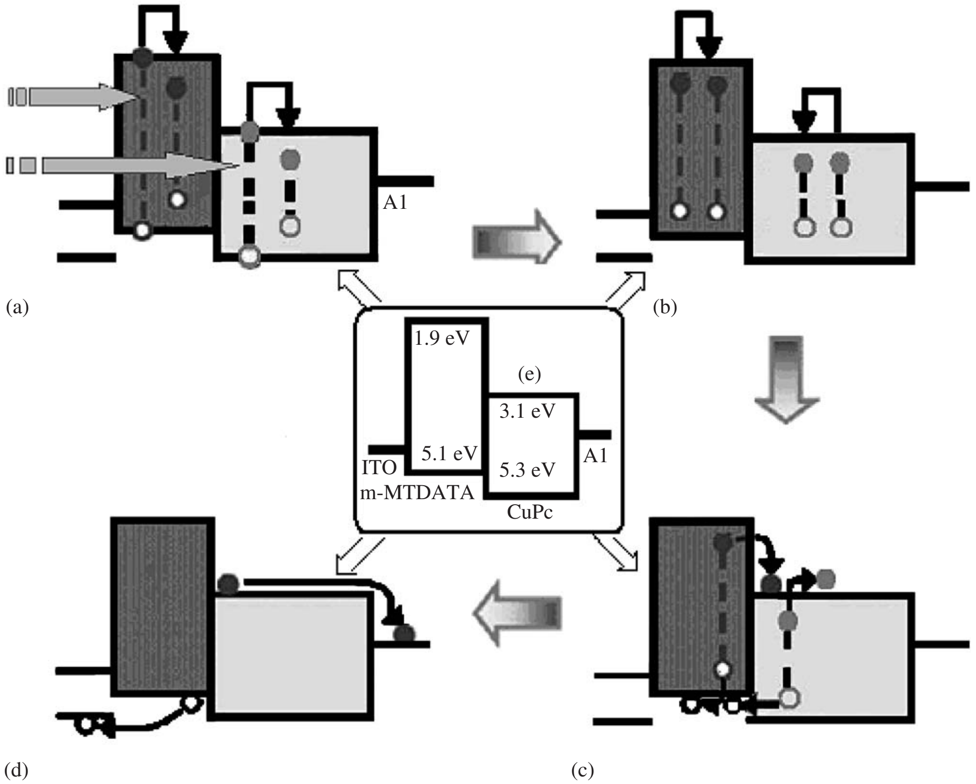


Fig. 5. Schematic illustration of the consecutive steps in the generation of photocurrent from incident light in m-MTDATA/CuPc heterojunction photovoltaic diode.

the electrodes (d). If the two terminals of the diode are connected through an external circuit, a photocurrent is generated [18]. And (e) refers to the energy level diagram of m-MTDATA/CuPc heterojunction photovoltaic diode.

Because energies of both LUMO (1.9 eV) and HOMO (5.1 eV) of m-MTDATA [10] is sufficiently higher than those of CuPc (3.1 and 5.3 eV) [13,14], respectively, it is energetically favorable for an exciton reaching D–A interface to dissociate, leaving a negative polaron on the acceptor and a positive polaron on the donor, respectively [13]. Additionally, because of lower IP (1.9 eV) and larger HOMO–LUMO energy gap (3.2 eV) of m-MTDATA, the device composed of m-MTDATA and CuPc has higher I_{sc} of 54.6 $\mu A/cm^2$ and V_{oc} of 1.05 V. However HOMO of TPD (5.5 eV) even lower than that of CuPc (5.3 eV), which is disadvantage for exciton reaching the interface and dissociating there, so device (b) has lower I_{sc} of 20 $\mu A/cm^2$ and open-circuit voltage V_{oc} of 0.88 V.

3.5. The effect of incident light intensities on I_{sc} and V_{oc}

Current density–voltage characteristics of the diode at different incident light intensities were investigated under 365 nm illumination as shown in Fig. 6(a), indicating that the I_{sc} is directly proportional to the incident UV intensity. The I_{sc} increases largely from

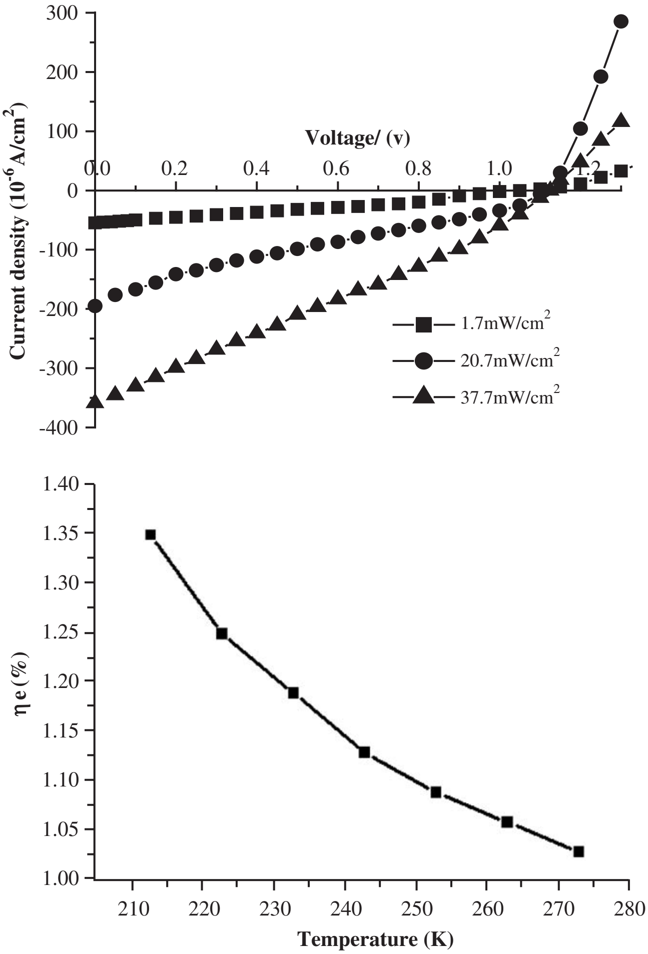


Fig. 6. (a) Current density–voltage characteristics of the diode at different incident light intensities with 365 nm wavelength, (b) power conversion efficiency of the diode at lower temperature.

54.6 μA/cm^2 at 1.7 mW/cm^2 to 358.8 μA/cm^2 at 37.7 mW/cm^2. At the same time, V_{oc} increases slightly with the incident UV light from 1.05 V at 1.7 mW/cm^2 to 1.125 V at 37.7 mW/cm^2. Such a diode can give different signal in quantity under different UV intensity. It can be applied to find out the intensity of the UV radiation in the sunshine from the detectors directly.

3.6. The effect of the temperature on η_e

In addition, PV diode should generally be used outdoor, so we investigated the variation of η_e with the temperature. As shown in Fig. 6(b), when the temperature decreases from 273 to 213 K [19] with a 10 K interval, the power conversion efficiency of device increases from 1.04% to 1.35%. The diode performance is presumably better at lower temperature, showing that the PV diode can be used even in cold circumstance, because the behavior at low temperature will be much better than that at room temperature.

4. Conclusion

In summary, organic PV diode based on CuPc as an electron acceptor has been designed and fabricated as an UV light sensor, which shows higher open-circuit voltage, and the performances increases largely with the increasing incident UV radiation and the reducing of the temperature. Ultraviolet (UV) radiations reaching the surface of the earth from solar are between wavelengths of 280–400 nm [20]. Long-term exposure to UV radiation causes prematurely aged skin, wrinkles, loss elasticity, dark patches and actual skin cancers. A simple and reusable device with credit card size would be useful for monitoring UV radiation intensity. This type of UV-light sensor can be used in cold place, giving different signal with varying the UV radiation intensity.

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